

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
9 August 2001 (09.08.2001)

PCT

(10) International Publication Number  
**WO 01/57164 A1**

- (51) International Patent Classification<sup>7</sup>: C10M 171/00, 107/34, 107/46
- (21) International Application Number: PCT/GB01/00251
- (22) International Filing Date: 23 January 2001 (23.01.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
0002260.8 2 February 2000 (02.02.2000) GB
- (71) Applicant (for all designated States except US): LA-  
PORTE PERFORMANCE CHEMICALS UK LIM-  
ITED [GB/GB]; Charleston Road, Hardley, Hythe,  
Southampton SO45 3ZG (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): LAWFORD, Simon  
[GB/GB]; 78 Primrose Gardens, Poole, Dorset BH17  
7BG (GB). MOXEY, John, Robert [GB/GB]; Forest  
Oak, Southampton Road, Landford, Salisbury, Wiltshire  
SP5 2BE (GB). SMALL, Andrew [GB/GB]; Westwood,  
Winsor Road, Winsor, Southampton SO40 2HR (GB).
- (74) Agent: SMITH, Julian, Philip, Howard; BP Interna-  
tional Limited, Patents & Agreements, Chertsey Road,  
Sunbury-on-Thames, Middlesex TW16 7LN (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,  
LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO,  
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,  
TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
- with international search report
  - before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments
- For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.



WO 01/57164 A1

(54) Title: LUBRICATING OILS COMPRISING POLYOXYALKYLENGLYCOL DERIVATES

(57) Abstract: A composition is disclosed which comprises a lubricating oil and a refrigerant, wherein the lubricating oil comprises a polyalkyleneglycol derivative of the formula (I):  $RX(R^aO)_x(R^bO)_y(R^cO)_zR^d$ , wherein: X = O or S, R is a C<sub>3</sub> to C<sub>15</sub> substituent comprising a heterocyclic ring, in which the heteroatom(s) in said ring is (are) oxygen and/or sulphur, R<sup>a</sup> is a C<sub>2</sub> alkylene group, R<sup>b</sup> is a C<sub>3</sub> alkylene group, R<sup>c</sup> is a C<sub>4</sub> alkylene group, R<sup>d</sup> is the same as R, or is H, a C<sub>1</sub>-C<sub>20</sub> alkyl or a C<sub>1</sub>-C<sub>20</sub> acyl, x, y, z are each independently 0 or an integer of 100 or less, and x + y + z = 4 to 100, but excluding compositions where the refrigerant is halogen-free and R contains a carbonate group. The use of borate esters as dehydrogenating agents in conjunction with the above lubricating oils is also disclosed.

## LUBRICATING OILS COMPRISING POLYOXYALKYLENGLYCOL DERIVATES

The present invention relates to a polyalkylene glycol derivative for use as a lubricating oil, and more particularly, for use as a lubricating oil in compression-type refrigerators.

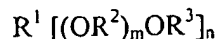
In a conventional compression-type refrigerator, a mixture of a refrigerant and a lubricating oil is circulated through a number of units including a compressor, which  
5       exerts pressure on the gaseous refrigerant to convert it into a liquid. Such units comprise moving parts, and the lubricating oil is necessary to reduce friction between these parts. In addition to such lubricating properties, it is desirable for the lubricating oil to be compatible with the refrigerant. This is because the temperatures encountered  
10       by the refrigerant/lubricating oil mixture may range from 65°C in the compressor, to -40 °C in the cooler. If the lubricating oil is incompatible with the refrigerant at any point within this temperature range, phase separation may occur, reducing the efficiency of the lubrication and refrigeration process.

Various lubricating oils for refrigerants are known. US 4755316, for instance,  
15       discloses lubricating oil compositions containing one or more polyether polyols. The composition is suitable for use with compression refrigerants, such as 1,1,1,2-tetrafluoroethane (R134a).

US 4851144 also describes lubricating oils which are suitable for refrigerants such as R134a. The lubricating oils of US 4851144 are based on mixtures of polyether  
20       polyols, and esters.

In EP 377122A and EP 634467A, a lubricating oil based on a derivative of polyoxyalkylene glycol is disclosed. One of the lubricating oils disclosed is represented

by the general formula:



wherein  $R^1$  is an alkyl group having 1 to 10 carbon atoms, an acyl group having 1 to 10 carbon atoms or an aliphatic hydrocarbon group having 2 to 6 valencies;

5  $R^2$  is an alkylene group having 2 to 4 carbon atoms;

$R^3$  is an alkyl group having 1 to 10 carbon atoms, or an acyl group having 1 to 10 carbon atoms,

$n$  is an integer of 1 to 6, and

$m$  is an integer of 1 to 80.

10 EP 913456A discloses lubricants for halogen-free refrigerants corresponding to the general formula above but where  $R^1$  is a 5-membered cyclic alkylene carbonate (ie containing an -O-(C=O)-O- group). There is no suggestion that they would have suitable solubility characteristics to enable them to be used with halogenated refrigerants as well.

15 We have now developed a new lubricating oil based on a derivative of polyoxyalkylene glycols having a heterocyclic substituent.

According to the present invention, there is provided a lubricating oil comprising a polyalkyleneglycol derivative of the formula (I):



20 wherein:

$X = O$  or  $S$ ,

$R$  is a  $C_3$  to  $C_{15}$  substituent comprising a heterocyclic ring, in which the heteroatom(s) in said ring is (are) oxygen and/or sulphur,

$R^a$  is a  $C_2$  alkylene group,

25  $R^b$  is a  $C_3$  alkylene group,

$R^c$  is a  $C_4$  alkylene group,

$R^d$  is the same as  $R$ , or is  $H$ , a  $C_1$ - $C_{20}$  alkyl or a  $C_1$ - $C_{20}$  acyl,

$x, y, z$  are each independently 0 or an integer of 100 or less, and

$x + y + z = 4$  to 100.

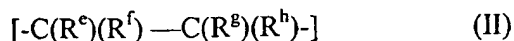
30  $X$  is preferably oxygen.

The products of the present invention have demonstrated a considerable advantage over commercially available dimethyl ethers (which are similar to those

described it in EP 634467), in that they show no separation at low temperatures. Modern compressors can work down to -60°C or below, and hence this has become an increasingly important aspect; low temperature separation in compression type refrigerators can result in incomplete carry through and circulation of the lubricant,  
 5 leading to wear problems and the like.

As mentioned above, R is a substituent comprising a C<sub>3</sub> to C<sub>15</sub> heterocyclic species, in which the heteroatom(s) in the heterocyclic ring is oxygen and/or sulphur. Preferably, the heterocyclic ring comprises oxygen or sulphur. The heterocyclic ring may be saturated or unsaturated. For example, R may comprise a saturated cyclic ether  
 10 or saturated cyclic thioether. Such cyclic compounds may or may not be substituted. When substituted, the heterocycle may be linked to X via the or a substituent, which in such a case may be a hydrocarbyl linkage, eg -CH<sub>2</sub>-, -C<sub>2</sub>H<sub>4</sub>- or -C<sub>3</sub>H<sub>6</sub>-. Preferably, R comprises a C<sub>4</sub> to C<sub>6</sub> heterocyclic moiety which is attached to X either directly or via a hydrocarbyl linkage. For example, the heterocyclic moiety may be a furan or a  
 15 thiophene ring. The heterocyclic moiety may alternatively be furfuryl, or a furfuryl derivative such as tetrahydrofurfuryl, attached to X either directly or via a hydrocarbyl linkage. Examples of compounds from which R may be derived include tetrahydrofuran, methyltetrahydrofuran, tetrahydrothiophene or methyltetrahydrothiophene substituents. A preferred example of R is derivable from 2-  
 20 hydroxymethyltetrahydrofuran, which may be regarded as having the formula R-XH according to the above definition, such that R is derived from methyltetrahydrofuran and X is O.

Each of R<sup>a</sup>, R<sup>b</sup> and R<sup>c</sup> may be represented by formula II:



25 In the case of R<sup>a</sup>, each of R<sup>e</sup>, R<sup>f</sup>, R<sup>g</sup>, and R<sup>h</sup> is hydrogen. In the case of R<sup>b</sup>, one of R<sup>e</sup>, R<sup>f</sup>, R<sup>g</sup>, and R<sup>h</sup> is methyl and the others are hydrogen. In the case of R<sup>c</sup>, either one of R<sup>e</sup>, R<sup>f</sup>, R<sup>g</sup>, and R<sup>h</sup> is ethyl or two of R<sup>e</sup>, R<sup>f</sup>, R<sup>g</sup>, and R<sup>h</sup> is methyl, the remainder being hydrogen. For example, R<sup>c</sup> may be a butylene group or an iso-butylene group.

Preferably, only one or two of R<sup>a</sup>, R<sup>b</sup> and R<sup>c</sup> are present in formula I. In other  
 30 words, in preferred embodiments of the invention one or two of x, y and z is zero. For example, x may be zero, and/or z may be zero.

R<sup>d</sup> may be the same as R, or may be an H, a C<sub>1</sub>-C<sub>20</sub> alkyl or a C<sub>1</sub>-C<sub>20</sub> acyl. Where

$R^d$  is a  $C_1$ - $C_{20}$  alkyl or a  $C_1$ - $C_{20}$  acyl group, it preferably has 1 to 15 carbon atoms, more preferably, 1 to 10 carbon atoms, and most preferably, 1 to 6 carbon atoms. Where  $R^d$  is a  $C_1$ - $C_{20}$  alkyl group, the alkyl group may be straight chain, branched chain or a cyclic alkyl group. Suitable alkyl groups include methyl, ethyl, propyl, butyl, pentyl, and hexyl groups. Where  $R^d$  is a  $C_1$ - $C_{20}$  acyl group, the acyl group may be straight chain, branched chain or cyclic. The acyl group may have further substituents, for example, alkyl substituents, which may be a straight chain, branched chain or cyclic alkyl substituent. Such alkyl substituents include methyl, ethyl, propyl, butyl, pentyl, and hexyl groups.

10  $x + y + z = 4$  to 100 (inclusive). Preferably, the sum is equal to a number between 5 and 50 (inclusive), more preferably, between 15 and 40, and most preferably, between 15 and 25. In one embodiment,  $x = 0$ ,  $z = 0$  and  $y = 18$ . In another embodiment,  $x = 0$ ,  $y = 17$  and  $z = 1$ .

The polyalkyleneglycol derivative of the formula (I) may be prepared by any suitable method known in the art. Suitable methods are described in Methods A, B and C described on pages 7 to 8 of EP 0634467. A preferred method, however, is described below.

A compound of the formula RXH (R and X as defined above) is employed as an initiator, and reacted with ethylene oxide, propylene oxide and/or butylene oxide. Ethylene oxide, propylene oxide or butylene oxide may each be used on its own, or mixtures of two or more of such alkylene oxides may be employed. Where two or more alkylene oxides are employed, these alkylene oxides may be reacted sequentially in any order. Thus, RXH may be reacted with one of ethylene oxide, propylene oxide, or butylene oxide, and the resulting product reacted with a different alkylene oxide selected from that list, or vice-versa. Optionally, the resulting product may be reacted further, for example, with yet a different alkylene oxide altogether, or alternatively, the same alkylene oxide that was used in the first addition step. In one embodiment, RXH is first polymerised with propylene oxide, and the resulting product is reacted with isobutylene oxide.

30 The initiator may be used either as RXH or as an alkali metal salt thereof. Examples of suitable initiators include 3-hydroxy tetrahydrofuran, 2-hydroxymethyltetrahydrofuran, 2-hydroxymethyltetrahydrothiophen, furfuryl alcohol,

2-hydroxymethyltetrahydropyran, and 3-hydroxyfuran.

The reaction is preferably catalysed by a base, a Lewis acid or a double metal cyanide. Suitable acids include boron trifluoride. Suitable bases include potassium hydroxide. The resulting product may comprise a polyalkyleneglycol derivative of the  
5 formula (I), wherein  $R^d$  is H.

Such a product may be further reacted using reactions known in the art, such that  $R^d$  is converted to an alkyl, an acyl group or to a group identical to R. For example, the product may be reacted with an alkyl chloride or dialkyl sulphate to produce a polyalkyleneglycol derivative of the formula (I), wherein  $R^d$  is an alkyl group.  
10 Alternatively, the product may be esterified either directly or indirectly to produce a polyalkyleneglycol derivative of the formula (I), wherein  $R^d$  is an acyl group. To obtain a product in which  $R^d$  is the same as R, the product may be reacted with for example, the appropriate chloride. For example, where R is derived from 2-hydroxymethyltetrahydrofuran, the product may be reacted with 2-(chloromethyl)-  
15 tetrahydrofuran. Alternatively, two equivalents of the product may be reacted with ethylene dibromide.

The lubricating oil of the present invention may be used as a lubricant for industrial, automotive and refrigeration/air-conditioning applications. For example, the oil may be used to lubricate gears, bearings and compression-type refrigerators. The  
20 present invention is very suitable for the latter application because it is highly compatible with refrigerants, such as fluorocarbons, hydrocarbons (e.g. propane), ammonia, and carbon dioxide. Of these refrigerants, the present invention has been found to be particularly useful for lubricating fluorocarbons such as 1,1,1,2-tetrafluoroethane (R134a), difluoromethane (R32), pentafluoroethane (R125) and 1,1,1-  
25 trifluoroethane (R143a) and blends thereof. The present invention may even improve the compatibility of other lubricating oils with such refrigerants. For this reason, the lubricating oil of the present invention may be blended with other lubricating oil(s) to produce a lubricating composition for such refrigerants.

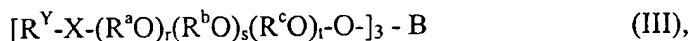
The lubricating oil may also be used in combination with other additives, such as  
30 extreme pressure, antiwear, anticorrosion, antioxidants, and viscosity improver additives. Other additives include acidity regulators, reactive water-eliminating additives, antifoams, and demulsifiers.

The lubricating oil of the present invention may have a viscosity of 2 to 50 cSt at 100°C. Preferably, the viscosity of the oil is 5 to 30cSt, more preferably, 6 to 30cSt, and most preferably, 9 to 30 cSt.

The lubricating oil of the present invention may be used in combination with a  
 5 dehydrating agent. Any suitable dehydrating agent may be employed. Dehydrating agents may be employed to reduce the water content of lubricating oils from typical values of 0.1 to 0.5wt % or more, to values of less than 0.05 wt %, for example, less than 0.015 wt %. This is an advantage because water tends to freeze and separate from the lubricating oil at temperatures below 0°C in the expansion bulb of the compressor.  
 10 This separation reduces the effectiveness of the lubrication

A number of conventional dehydrating agents are known. Typically, these are heterogeneous agents, such as molecular sieves, which have to be incorporated into the compressor design. Although such agents may be effective, they add complexity to the compressor design. Accordingly, it is desirable to use homogeneous chemical  
 15 dehydrating agents, which can simply be blended with the lubricating oil.

We have found that certain borate esters, in particular, those falling within the definition of Formula III below have useful dehydrating characteristics:



wherein X = O or S,

20  $R^Y$  is a  $C_1$ - $C_{10}$  alkyl, or a  $C_3$  to  $C_{15}$  substituent comprising a heterocyclic ring, in which the heteroatom(s) in said ring is (are) oxygen and/or sulphur,

$R^a$  is a  $C_2$  alkylene group,

$R^b$  is a  $C_3$  alkylene group,

$R^c$  is a  $C_4$  alkylene group,

25 r, s, t are each independently 0 or an integer of 50 or less, and

$r + s + t = 3$  to 50 (inclusive).

Where  $R^Y$  is a  $C_1$  to  $C_{10}$  alkyl, both straight chained and branched alkyl substituents may be employed.  $C_1$  to  $C_6$  alkyls are preferred. Suitable examples include methyl, propyl, butyl, pentyl, and hexyl. Preferably,  $R^Y$  is methyl.

30  $R^Y$  may also have the same meaning as R above.

The  $R^Y$  group may be derived from an  $R^YXH$  initiator.

As described in connection with Formula I,  $R^a$ ,  $R^b$  and  $R^c$  may each be derived

from alkylene oxides. In the preparation of the borate ester III, such alkylene oxides may be reacted with  $R^YXH$  initiators. Where two or more  $R^a$ ,  $R^b$  and  $R^c$  groups are present, a mixture of two or more alkylene oxides may be reacted with the initiator. It is possible, however, to react different alkylene oxides sequentially in separate reaction steps.

The present invention provides in a further aspect a composition comprising a refrigerant, a lubricating oil, and a borate ester of the formula (III). As the borate ester III itself possesses lubricant properties, it may be used in any proportion. Preferably, however, the ester III forms 1 to 25 wt % of the lubricating oil/ester mixture (excluding the refrigerant).

The invention also includes in another aspect the use of a borate ester of the formula (III) as a dehydrating agent for a lubricating oil used in conjunction with a refrigerant. Preferably the lubricating oil is of the formula (I).

Preferably, the lubricating oil/borate ester composition of the present invention comprises 50 to 99 wt % of the lubricating oil. More preferably, the composition comprises 95 to 100 wt % of the lubricating oil. The composition may also comprise additives such as antioxidant, antiwear, extreme pressure, anti-corrosion and acidity scavenger additives. Typically, however, such additives only form 0.1 to 5 wt % of the total weight of the composition.

The borate ester of Formula III may be prepared by the reaction of a polyalkylene glycol with boric acid. The water of reaction may then be removed by distillation.

It has also been found that the borate ester of Formula III itself has good lubricating properties. Furthermore, the ester (III) has been found to be highly compatible with refrigerants, such as fluorocarbons, hydrocarbons (eg propane), ammonia, and carbon dioxide. Of these refrigerants, the ester (III) has been found to be particularly useful for lubricating fluorocarbons such as 1,1,1,2-tetrafluoroethane (R134a), difluoromethane (R32), pentafluoroethane (R125) and 1,1,1-trifluoroethane (R143a) and blends thereof. Accordingly, another aspect of the present invention is the use of the borate ester of the formula III above as a lubricating oil for such refrigerants.

These and other aspects of the present invention will now be described by way of illustration with reference to the following Examples:

Example 1

2-hydroxymethyltetrahydrofuran was used as the initiator (RXH). This compound was reacted with propylene oxide under the reaction conditions described below. Both the intermediate and the final product formed in this example fall within the definition of Formula I above. However, whereas the intermediate had a y value of about 9, the y value of the final product was about 18. The x and z values of both the intermediate and final products were respectively zero.

2-hydroxymethyltetrahydrofuran (1062g) was charged into a 10 litre pressure reactor. 24.3g of potassium methoxide was then added, this amount being necessary to give a concentration of 0.20% in the final product.

Propylene oxide (5000g) was then added to the reactor at a reaction temperature of 120°C on an automatic demand system. After reacting to constant pressure, an intermediate (3152g) was removed. This intermediate had a hydroxyl number of 99.1 mg. KOH / g.

To the remaining 2934g in the reactor, a further 2885g propylene oxide was added, also at 120°C, to give the final product which, after treatment with magnesium silicate to remove the catalyst, had a hydroxyl number of 52.3. This hydroxyl number is indicative of a y value of 18. This product had a viscosity at 40°C of 58.4 cSt, with a pH of 6.6, a water content of 0.03%, and colour of 30 Hazen. The viscosity at 100°C was 10.7 cSt.

Example 2

In this Example, the final product of Example 1 was reacted with isobutylene oxide. The resulting product was found to have a y value of 17 and a z value of 1.

A second sample product made as in Example 1 (4.7 kg, hydroxyl number of 55.8) was reacted with isobutylene oxide (400g, 1 mole) at 120°C. After removal of catalyst, the product (5.1 kg) had the following properties.

	Hydroxyl No. (mgKOH/g)	12.8
	Viscosity @ 40°C (cSt)	57.6
	Water (%)	0.02
30	PH (IPS/Water)	6.9
	Colour (Pt/Co)	50
	Appearance	Clear

Example 3

In this Example, the final product of Example 1 was capped with a methyl group, such that R<sup>d</sup> was methyl.

3000g of the final product of Example 1 was reacted with 756g (1.25 equivalents) sodium methoxide in vacuo at 90°C for four hours. 282g (2 equivalents) methyl chloride was then added to the mixture at 90°C for four hours. The product was then acidified with aqueous hydrochloric acid to pH 5, and washed with water to remove salts. The product was separated and treated with magnesium silicate, filtered and dried. The resulting capped material had a residual hydroxyl of 5.3 (90% capped), a viscosity at 40°C of 42.9, a viscosity at 100°C of 9.2, giving a viscosity index of 204.

Example 4

In this example, a borate ester falling within the definition of Formula III above was synthesised.

A propoxylate of methanol (300g) with a hydroxyl number of 50 (Mw 1122), viscosity = 55cSt @ 40°C was mixed together with orthoboric acid (Mw 62) (5.5g). The reactants were mixed with 100 ml of toluene, and the mixture heated at reflux using a Dean Stark apparatus, until water of reaction and water from the reagents had been removed (1.6g and 2.4g) and no further water separated. The solvent was then removed in vacuo to leave approximately 300g of the borate triester.

Example 5

In this Example, the lubricating oil produced in Example 3 was blended with the borate ester of Example 4 to produce a composition according to an embodiment of the present invention.

10 grams of the product of Example 4 were mixed with 100g of the product of Example 3. The resulting mixture was analysed and found to have a water content of 0.0wt %. The water content of the unblended lubricating oil (Example 3) was measured at 0.1wt %.

Examples 6 - 14

Further polyalkylene glycols of differing molecular weights using different heterocyclic initiators were prepared according to the method of Example 1.

To the PAG was added 25% sodium methoxide (1.1 molar equivalent). The methanol was then removed by distillation; the temperature was slowly increased to

- 100°C following which the vacuum was increased to 10mbar. After 4 hours stripping under these conditions, the mixture was returned to atmospheric pressure using nitrogen gas. Methyl chloride (1.2 molar equivalents) was gently bubbled into the mixture at 85-90°C over a three-hour period. The reaction mixture was then poured into a separating
- 5 funnel and washed four times with 0.2 volumes of saturated brine. The product was finally dried at 100° for two hours and filtered to obtain the desired capped PAG. A summary of the polyalkylene glycols produced is shown in Table 1 below.

TABLE 1

Ex. No	<u>Propoxylate Initiator</u>	Cap (R <sup>d</sup> )	Starting OH No.	End OH No.	Capping (%)	Viscosity after capping, cSt.
6	Furfuryl alcohol	methyl	64.7	3.8	94.1	50.4 (40°C) 9.1 (100°C)
7	THPM	methyl	64.5	4.7	92.7	
8	THFA	acetyl	52.3	6.8	87.0	
9	THFA	methyl	27.0	2.0	92.6	159.0 (40°C)
10	THFA	methyl	32.1	1.5	95.3	100.7 (40°C)
11	THFA	methyl	66.5	1.0	98.5	28.6 (40°C)
12	THFA	methyl	82.5	5.2	93.7	20.4 (40°C)
13	THFA	methyl	105	4.6	95.6	13.5 (40°C)
14 <sup>#</sup>	Propylene glycol	methyl	-	-	-	46
# Comparative Example: commercial product of Idemitsu Kosan Co - polypropylene glycol with both hydroxyl groups methyl capped.						
THFA = 2-hydroxymethyltetrahydrofuran, THPM = 2-hydroxymethyltetrahydropyran						

#### 10 Low-temperature separation tests

As described previously, good low-temperature separation properties are an important requirement for lubricants used in modern compressors. The product of Example 3 was compared with that of comparative Example 14. Example 14 is a product of Idemitsu Kosan Co and is of a chemical nature identical or very similar to

that of Example 8 of EP 377122A. It is the most similar to Example 3 in terms of viscosity, upper clouding temperature, and the linearity of chain structure.

In the test, the lubricant and the fluorocarbon refrigerant are sealed in a tube and cooled.

The temperature of any separation is observed. High-temperature separation can also

- 5 be evaluated by heating the tube and observing. The results for the low-temperature separation are shown in Table 2 below. They show that the product of Example 3 does not separate even at the lowest temperature tested of -60°C. However, comparative Example 14 separates at much higher temperatures.

TABLE 2

Concentration in refrigerant (R134a)	Temperature of separation at low temperature			
	5%	10%	30%	40%
Product of comparative Example 14	-41°C	-39°C	39°C	-40°C
Product of Example 3	< - 60 °C	< - 60 °C	< - 60 °C	< - 60 °C

10

Although certain examples in EP 377122A show lower separation temperatures, they are not directly comparable as they are generally not linear. The linear structures are the preferred commercial products, because they have the advantage of higher viscosity index, lower cost of capping, and can be made to the molecular weight

- 15 requirements of very low viscosity now being demanded in energy saving compressors.

20

25

## Claims

1. Composition comprising a lubricating oil and a refrigerant, wherein the lubricating oil comprises a polyalkyleneglycol derivative of the formula (I):



wherein:

- 5 X = O or S,

R is a C<sub>3</sub> to C<sub>15</sub> substituent comprising a heterocyclic ring, in which the heteroatom(s) in said ring is (are) oxygen and/or sulphur,

R<sup>a</sup> is a C<sub>2</sub> alkylene group,

R<sup>b</sup> is a C<sub>3</sub> alkylene group,

- 10 R<sup>c</sup> is a C<sub>4</sub> alkylene group,

R<sup>d</sup> is the same as R, or is H, a C<sub>1</sub>-C<sub>20</sub> alkyl or a C<sub>1</sub>-C<sub>20</sub> acyl,

x, y, z are each independently 0 or an integer of 100 or less, and

x + y + z = 4 to 100, but excluding compositions where the refrigerant is halogen-free and R contains a carbonate group.

- 15 2. Composition according to claim 1 wherein R comprises a C<sub>4</sub> to C<sub>6</sub> heterocyclic moiety which is attached to X either directly or via a hydrocarbyl linkage.

3. Composition according to claim 1 or 2 wherein R is derived from tetrahydrofuran, methyltetrahydrofuran, tetrahydrothiophene, methyltetrahydrothiophene, furfuryl or tetrahydrofurfuryl.

- 20 4. Composition according to any preceding claim wherein each of R<sup>a</sup>, R<sup>b</sup> and R<sup>c</sup> is represented by the formula  $[-C(R^e)(R^f)-C(R^g)(R^h)-]$

wherein:

in the case of R<sup>a</sup>, each of R<sup>e</sup>, R<sup>f</sup>, R<sup>g</sup>, and R<sup>h</sup> is hydrogen;

in the case of  $R^b$ , one of  $R^c$ ,  $R^f$ ,  $R^g$ , and  $R^h$  is methyl and the others are hydrogen;  
 in the case of  $R^c$ , either one of  $R^c$ ,  $R^f$ ,  $R^g$ , and  $R^h$  is ethyl, or two of  $R^c$ ,  $R^f$ ,  $R^g$ , and  $R^h$  are methyl, the remainder being hydrogen.

5. Composition according to any preceding claim wherein one or two of x, y and z is zero.
6. Composition according to any preceding claim wherein  $R^d$  is methyl, ethyl, propyl, butyl, pentyl, hexyl or acyl optionally substituted with methyl, ethyl, propyl, butyl, pentyl, or hexyl groups.
7. Composition according to any preceding claim wherein  $x + y + z = 5$  to 50, preferably 15 to 40, and more preferably, 15 to 25.
8. Composition comprising a refrigerant, a lubricating oil, and a borate ester of the formula (III)
 
$$[R^Y-X-(R^aO)_r(R^bO)_s(R^cO)_t-O-]_3 - B \quad (III),$$
 wherein  $X = O$  or  $S$ ,
  - 15  $R^Y$  is a  $C_1$ - $C_{10}$  alkyl, or a  $C_3$  to  $C_{15}$  substituent comprising a heterocyclic ring, in which the heteroatom(s) in said ring is (are) oxygen and/or sulphur,
  - $R^a$  is a  $C_2$  alkylene group,
  - $R^b$  is a  $C_3$  alkylene group,
  - $R^c$  is a  $C_4$  alkylene group,
  - 20  $r, s, t$  are each independently 0 or an integer of 50 or less, and  $r + s + t = 3$  to 50 (inclusive).
9. Composition according to claim 8 wherein  $R^Y$  is methyl, propyl, butyl, pentyl, or hexyl.
10. Composition according to claim 8 or 9 wherein the borate ester is the reaction product of orthoboric acid and a propoxylate of methanol.
- 25 11. Composition according to any of claims 8 to 10 wherein the borate ester of the formula (III) is present in an amount of from 1 to 25 wt % based on lubricating oil plus ester only.
12. Composition according to any of claims 8 to 10 wherein the lubricating oil is as defined in any of claims 1 to 7.
- 30 13. Composition according to any preceding claim wherein the refrigerant comprises 1,1,1,2-tetrafluoroethane (R134a), difluoromethane (R32), pentafluoroethane (R125) or 1,1,1-trifluoroethane (R143a) or blends thereof.

14. Use of a borate ester of the formula (III) as a dehydrating agent for a lubricating oil used in conjunction with a refrigerant.

5

10

15

20

25

30

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/00251

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10M171/00 C10M107/34 C10M107/46 C10M139/00 C10M169/04  
C08G65/26 C09K5/04 //(C10M169/04, 107:34, 107:46, 139:00),  
C10N30:00, C10N40:30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M C08G C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 460 613 A (NIPPON OIL CO LTD) 11 December 1991 (1991-12-11) page 2, line 49 -page 4, line 15 ---	1,2,4-7
X	EP 0 711 824 A (NIPPON OIL CO LTD) 15 May 1996 (1996-05-15) page 3, line 40 -page 6, line 33 ---	1,2,4-7
A	EP 0 913 456 A (MATSUSHITA ELECTRIC IND CO LTD) 6 May 1999 (1999-05-06) cited in the application the whole document ---	1
A	EP 0 504 410 A (MITSUI PETROCHEMICAL IND) 23 September 1992 (1992-09-23) page 3, line 25 - line 29 --- -/--	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

27 June 2001

Date of mailing of the international search report

05.07.2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Rotsaert, L

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/00251

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 15551 A (LUBRIZOL CORP) 17 October 1991 (1991-10-17) page 3, paragraph 4 page 6, paragraph 3 page 7, paragraph 3 page 10, paragraph 1	8-10,13
A	page 22, paragraph 2 -page 23, paragraph 1 ---	11,12,14
X	PATENT ABSTRACTS OF JAPAN vol. 008, no. 118 (C-226), 31 May 1984 (1984-05-31) & JP 59 029625 A (NITSUSOU YUKA KOGYO KK), 16 February 1984 (1984-02-16) abstract ---	8-10,13
A	EP 0 582 451 A (NIPPON OIL CO LTD) 9 February 1994 (1994-02-09) page 2, line 44 - line 57 page 3, line 39 - line 51 page 5, line 32 - line 45 ---	8
A	WO 98 38264 A (SHIBANUMA TAKASHI ;IDE SATOSHI (JP); DAIKIN IND LTD (JP); TSUCHIYA) 3 September 1998 (1998-09-03) the whole document -----	8,14

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 01/00251

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-7

compositions comprising a refrigerant and a lubricating oil comprising a polyalkyleneglycol derivative.

2. Claims: 8 -14

compositions comprising a refrigerant, a lubricating composition and a borate ester and the use of said borate ester as a dehydrating agent.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/00251

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0460613 A	11-12-1991	JP 2901012 B JP 4041591 A	02-06-1999 12-02-1992
EP 0711824 A	15-05-1996	BR 9505108 A CA 2162229 A JP 8239679 A KR 164650 B US 5746933 A	09-09-1997 08-05-1996 17-09-1996 15-01-1999 05-05-1998
EP 0913456 A	06-05-1999	CN 1218821 A JP 2000008063 A	09-06-1999 11-01-2000
EP 0504410 A	23-09-1992	JP 2979526 B JP 4136031 A JP 2901734 B JP 4139154 A JP 4142330 A JP 5032688 A DE 69130760 D DE 69130760 T US 5294356 A AT 175659 T CA 2068878 A CN 1060478 A, B EP 0877013 A ES 2129410 T WO 9205140 A KR 9508087 B US 5476602 A US 5565129 A JP 5032588 A	15-11-1999 11-05-1992 07-06-1999 13-05-1992 15-05-1992 09-02-1993 25-02-1999 22-07-1999 15-03-1994 15-01-1999 18-03-1992 22-04-1992 11-11-1998 16-06-1999 02-04-1992 25-07-1995 19-12-1995 15-10-1996 09-02-1993
WO 9115551 A	17-10-1991	US 5094768 A AU 630848 B AU 7586491 A BR 9105672 A CA 2054691 A EP 0474832 A JP 4506542 T MX 172639 B NO 914662 A	10-03-1992 05-11-1992 30-10-1991 02-06-1992 01-10-1991 18-03-1992 12-11-1992 04-01-1994 27-11-1991
JP 59029625 A	16-02-1984	NONE	
EP 0582451 A	09-02-1994	DE 69315637 D DE 69315637 T JP 6100882 A US 5512198 A	22-01-1998 10-06-1998 12-04-1994 30-04-1996
WO 9838264 A	03-09-1998	EP 0974633 A	26-01-2000